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## Preparation of $MoO_3/CuMoO_4$ nanoparticles as selective catalyst for olefin epoxidation

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polymer; Molybdenum; Epoxidation; Catalyst. Abstract. Thermolysis of the mixture of  $[CuMoO_4(N_2C_{12}H_8)]$ .H<sub>2</sub>O and  $[Cu_3^{I}Cl(4,4'-bipy)_4][Cu^{II}(1,10-phen)_2Mo_8 O_{26}]$  (4,4'-bipy=4,4'-bipyridine and 1,10-phen=1,10-phenanthroline) coordination polymers has led to the formation of MoO<sub>3</sub>/CuMoO<sub>4</sub> nanoparticles (NPs). The nanomaterial was characterized by means of X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) analysis, Dynamic Light Scattering (DLS), and Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The MoO<sub>3</sub>/CuMoO<sub>4</sub> NPs were employed as heterogeneous catalysts in the epoxidation of olefins and allylic alcohols with *tert*-butyl hydroperoxide (TBHP) or cumene hydroperoxide (CHP) as oxidants in different solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>CN. The resulting catalyst displayed high activity and selectivity towards the epoxidation of olefins and allylic alcohols.

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#### 1. Introduction

Metal oxide nanoparticles are becoming a progressively important group of materials with potential applications in different research areas such as catalysis, magnetism, sensors, and optics [1-3]. Various methods have been devised to prepare metal oxide nanomaterials including solvothermal [4], co-precipitation [5], microwave synthesis [6], sol-gel process [7], chemical vapor methods [8], and template synthesis [9].

Decomposition of coordination polymers and Metal-Organic Frameworks (MOFs) is a facile and reasonable procedure to obtain desired metal oxide nanomaterials with diverse morphologies [10-12]. For instance,  $Co_3O_4$  nanoparticles were prepared by direct calcination of  $\{Co_3 \ (2,6\text{-NDC})_3(\text{DMF})_4\}_n$ (NDC= 2,6-naphtalene-dicarboxylate; DMF=N,N'- dimethylformamide) MOF [13]; nanostructured CuO was synthesized using  $Cu(C_6H_4NO_2)_2(H_2O)_4$ nanosheets and  $[Cu(C_6H_4NO_2)(OH)].H_2O(C_6H_4NO_2)$ = isonicotinic acid) nanorods [14]; MnO<sub>2</sub> nanowires were obtained from {Mn(SO<sub>4</sub>)(4,4-bipyirdine) (H<sub>2</sub>O)<sub>2</sub>}<sub>n</sub> MOF [15]; flowerlike NiO nano- materials were acquired from Ni<sub>3</sub>(btc)<sub>2</sub>.12H<sub>2</sub>O (btc=1,3,5benzen-tricarboxylic acid) [16]; ZnO nanorods were synthesized from 1-D coordination polymer [Zn(4,4bipyridine)Cl<sub>2</sub>], while nanoneedle-like ZnO was formed from thermolysis of [Zn(C<sub>2</sub>O<sub>4</sub>)(4,4-bipyridine)] [17].

Among metal oxide materials, molybdenum-based oxides are important from catalytic point of view since they serve as effective catalysts for industrial reactions such as hydrodesulphurization of petrol, hydrogenation, oxidation, polymerization, and metathesis of olefins [18,19]. For example,  $CeO_2-MoO_3/SiO_2$ was exploited as a catalyst for the oxidative coupling of benzylamines to N-benzylbenzaldimines, which is recognized as an industrially important reaction [20]. It was also reported that molybdenum oxide can act

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as a promoter in the acetalization of glycerol with ketones or aldehydes which presumes significant importance from industrial and environmental aspects [21-24]. Additionally, molybdenum-based materials are excellent catalysts for the epoxidation of olefins that is a crucial reaction in both industry and academia since epoxides are proper intermediates that can form a variety of other compounds [25,26]. In this association, we have studied the catalytic activity of molybdenumbased catalysts for the epoxidation of olefins [27-29].

Synthesis of molybdenum oxide materials as effective epoxidation catalysts [30-34] provoked us to prepare  $MoO_3/CuMoO_4$  nanoparticles through the thermolysis of the mixture of  $[CuMoO_4(N_2C_{12}H_8)]$ .H<sub>2</sub>O and  $[Cu_3^ICl(4,4'-bipy)_4][Cu^{II}(1,10-phen)_2 Mo_8O_{26}]$  (4,4'-bipy=4,4'-bipyridine and 1,10-phen = 1,10-phenanthroline) coordination polymers. We have applied the nanosized  $MoO_3/CuMoO_4$  crystals as heterogeneous catalysts for the epoxidation of olefins and allylic alcohols. Moreover, the type of solvent and oxidant in the catalytic activity of the nanoparticles was explored.

#### 2. Experimental section

#### 2.1. Materials and instrumentation

All chemicals were acquired from commercial sources and used as received. X-Ray Diffraction (XRD) patterns of the samples were recorded on a Philips PW1800 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The Scanning Electron Microscopy (SEM, KYKY EM-3200) was used to examine the morphology of the samples. Elemental analyses were conducted by a scanning electron microscope with EDX (Energy Dispersive X-ray) detector INCA Penta FETx3. Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 8000) was employed to determine the metal content of the samples.

#### 2.2. Synthesis of $MoO_3/CuMoO_4$ NPs

The MoO<sub>3</sub>/CuMoO<sub>4</sub> NPs were prepared via thermolysis of [CuMoO<sub>4</sub>(1,10-phen)].H<sub>2</sub>O and ([Cu<sup>I</sup><sub>3</sub>Cl(4,4'-bipy)<sub>4</sub>][Cu<sup>II</sup>(1,10-phen)<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>]) (4,4'-bipy = 4,4'-bipyridine and 1,10-phen = 1,10-phenanthroline) coordination polymers at 600°C for 2 h. The coordination polymers were obtained based on a reported hydrothermal procedure [35]. In order to prepare the polymers, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O (0.1 mmol, 0.124 g), CuCl<sub>2</sub>.2H<sub>2</sub>O (0.3 mmol, 0.052 g), 4,4'-bipy (0.3 mmol, 0.047 g), 1,10-phenanthroline (0.2 mmol, 0.036 g), and KF (0.3 mmol, 0.017 g) were added to a Teffon-lined stainless steel autoclave containing H<sub>2</sub>O (10 ml) and stirred for 30 min. After adjusting the pH value of the mixture by diluted ethylenediamine to 5.5, the autoclave was sealed and heated at 165°C for 4 days.

The crystals containing the mixture of the coordination polymers were isolated by filtration, washed with distilled water, and annealed at  $600^{\circ}$ C for 2 h.

# 2.3. Epoxidation of olefins in the presence of $MoO_3/CuMoO_4$ NPs

Epoxidation of olefins and allylic alcohols was conducted using *tert*-butyl hydroproxide (TBHP, 70% in water) as oxidant. TBHP was dried using  $CH_2Cl_2$ according to the procedure mentioned in the literature [36]. *Tert*-butyl hydroproxide (TBHP, 14.4 mmol) as oxidant was added to a mixture of catalyst (100 mg) and substrate (8 mmol) in chloroform (10 ml). The mixture was refluxed at 60°C for a particular time, and the products were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a Flame Ionization Detector (FID). GC-MS (Gas Chromatography-Mass Spectrometry) of the products was acquired using a Shimadzu-14A with a capillary column (CBP5-M25).

#### 3. Results and discussion

#### 3.1. Characterization of $MoO_3/CuMoO_4$ catalyst

The MoO<sub>3</sub>/CuMoO<sub>4</sub> NPs were formed by thermal decomposition of the mixture of  $[CuMoO_4(N_2C_{12}H_8)]$ . H<sub>2</sub>O and  $[Cu_3^{I}Cl (4,4'-bipy)_4][Cu^{II}(1,10-phen)_2Mo_8O_{26}]$  coordination polymers. The polymers were characterized by X-ray single crystal analysis [35]. The XRD pattern of the nanoparticles, illustrated in Figure 1, proves the formation of MoO<sub>3</sub> (JCPDS No. 05-0508) and CuMoO<sub>4</sub> (JCPDS No. 22-0242). The size of the particles was calculated from the peaks in the XRD patterns by means of Debye-Scherrer equation as seen below:

$$d = (0.89\lambda/\beta\cos\theta),\tag{1}$$

where d expresses the mean size of the particles,  $\lambda$  is the X-ray wavelength (1.5406 Åfor Cu K $\alpha$ ),  $\beta$  is the Full Width at Half Maximum (FWHM) of the peaks,



Figure 1. X-ray diffraction patterns of  $MoO_3/CuMoO_4$  nanocatalyst.

and  $\theta$  is the Bragg angle. The average crystal size is calculated to be about 22 nm.

The SEM micrograph of  $MoO_3/CuMoO_4$  NPs is provided in Figure 2(a), where the particles have spherical morphology with the size of 20-50 nm in diameter. The NPs were dispersed in water upon sonication, and their size distribution was identified by DLS analysis (Figure 2(b)). The result demonstrates that the size of the NPs is about 15-40 nm with a polydispersity index (PDI) of 0.255. As represented in Figure 2(c), chemical analysis, using EDX, displays the presence of molybdenum, copper, and oxygen in the sample.

#### 3.2. Catalytic activity studies

The research on the catalytic activity of MoO<sub>3</sub>/CuMo  $O_4$  NPs was carried out in the epoxidation of olefins and allylic alcohols. 3-methyl-2-butene-1-ol was designated as the typical substrate for the exploration of the epoxidation reaction using different solvents When TBHP or CHP and oxidants (Figure 3). was used as oxidant,  $MoO_3/CuMoO_4$  NPs showed more activity in  $CH_2Cl_2$  and  $CHCl_3$  in comparison to when  $CH_3CN$  was used as solvent. The reason could be more coordination ability of CH<sub>3</sub>CN and its tendency to fill the coordination sites of the catalyst. Based on Figure 3, it can be seen that the catalytic reaction can give better epoxidation conversions in the presence of TBHP in comparison with CHP due to more electrophilic nature of the peroxidic oxygen in TBHP. These observations that are well matched



Figure 3. The investigation of oxidant and solvent nature for the epoxidation. Reaction conditions:  $MoO_3/CuMoO_4$  catalyst (100 mg), 3-methyl-2-butene-1-ol (8 mmol), oxidant (14.4 mmol), refluxing solvent (10 ml), and temperature (solvent's boiling point).

with the previous reports [27,35] indicate that the use of TBHP as oxidant and non-coordinating solvents, such as chloroform or dichloromethane, results in more reactivity of  $MoO_3/CuMoO_4$  NPs. Therefore, the epoxidation reaction for the other substrates was accomplished in CHCl<sub>3</sub> using TBHP. The results for the catalytic epoxidation of the selected olefins and allylic alcohols indicate high activity of the catalyst (Table 1). The  $MoO_3/CuMoO_4$  nanocatalyst and its previously reported coordination polymer precursors exhibit good catalytic activity [35].



Figure 2. (a) SEM image, (b) DLS, and (c) EDX of MoO<sub>3</sub>/CuMoO<sub>4</sub> nanoparticles.

Entry	Substrate	Time (h)	Conversion <sup>a</sup> (%)	Selectivity <sup>b</sup> (%)
1	Cyclooctene	4	86	> 99
2	$\operatorname{Cyclohexene}$	24	96	> 99
3	Norbornene	6	92	> 9 9
4	trans-Stilbene	6	96	> 9 9
5	cis-Stilbene	2	100	> 99
6	1-Hexene	24	71	> 9 9
7	3-methyl-2-butene-1-ol	4	100	> 99
8	Allyl alcohol	2	100	> 99

Table 1. Catalytic epoxidation of olefins and allylic alcohols using MoO<sub>3</sub>/CuMoO<sub>4</sub> NPs.

Reaction conditions: catalyst (100 mg), olefins or allyl alcohols (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml), temperature (60°C).

<sup>a</sup>: Gc yield based on starting substrate.

<sup>b</sup>: Selectivity toward the formation of epoxide determined by GC-Mass.



**Figure 4.** Effect of time on 3-methyl-2-butene-1-ol conversion. Reaction conditions: catalyst (100 mg), substrate (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml), and temperature (60°C).

As displayed in Figure 4, 3-methyl-2-butene-1ol has rapidly undergone the epoxidation reaction utilizing  $MoO_3/CuMoO_4$  NPs within 30 min, and then is mostly oxidized after 4 h. To elucidate the catalytic efficiency of the prepared  $MoO_3/CuMoO_4$ nanomaterial, the reaction was accomplished without the catalyst using TBHP as oxidant and CHCl<sub>3</sub> as solvent, and low conversion (28%) was obtained after 2 h.

The recyclability of  $MoO_3/CuMoO_4$  catalyst was explored in the epoxidation of 3-methyl-2-butene-1-ol for four catalytic cycles within various reaction times. After each catalytic test, the catalyst was isolated, washed with CHCl<sub>3</sub> completely, and then reused in the



Figure 5. Kinetic profile of the epoxidation reaction in the presence of recycled MoO<sub>3</sub>/CuMoO<sub>4</sub>. Reaction conditions: recycled catalyst (100 mg), 3-methyl-2-butene-1-ol (8 mmol), TBHP (14.4 mmol), refluxing chloroform (10 ml), and temperature (60°C).

next experiment under the same reaction conditions. The results for the performance of the recycled catalyst are given in Figure 5. The catalytic activity was found almost the same as that of fresh catalyst after 5 hours without observable decrease in the activity after four cycles. These results were in good agreement with ICP-OES analysis for which no distinguishable loss of the metal content was observed after four consecutive catalytic cycles (Table 2). Furthermore, the XRD patterns of the fresh and recycled catalyst provided in Figure 1 are almost the same, implying that the catalyst is stable during the epoxidation reaction.

Table 2. Metal content of the catalyst obtained by ICP-OES analysis.

	Fresh MoO <sub>3</sub> /CuMoO <sub>4</sub> NPs	Recycled MoO <sub>3</sub> /CuMoO <sub>4</sub> NPs
Mo content (%)	36	33
Cu content (%)	21	19

#### 4. Conclusion

In the present work, direct calcination of the mixture of two coordination polymers led to the formation of  $MoO_3/CuMoO_4$  NPs. The catalytic potential of the NPs was explored in the epoxidation of some olefins and allylic alcohols. The prepared NPs served as heterogeneous catalyst and displayed high activity and selectivity in the epoxidation reaction. The nanocatalyst could be separated by filtration and reused for at least four catalytic cycles without noticeable change in its activity.

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